EQL Memo No. 15

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ACKNOWLEDGMENT

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The author wishes to thank Anna Pechanec and Betsy Krieg for research assistance on this project. Thanks is also due to the staff of the Los Angeles Air Pollution Control District for cooperation and assistance in furnishing data for this analysis. Valuable advice on data handling procedures was furnished by Dr. R. C. Y. Koh.

NOTE TO CONFERENCE PARTICIPANTS

This is a condensed version of materials presented at the Conference on Strategies for Air Pollution Control in the South Coast Air Basin, December 2-3, 1975. Remarks presented at that meeting concerning the automotive aspects of Los Angeles sulfate air quality are published separately as "Lead as a Tracer for Automotive Particulates: Projecting the Sulfate Air Quality Impact of Oxidation Catalyst Equipped Cars in Los Angeles," Environmental Quality Laboratory Memorandum No. 12.

ABSTRACT

Sulfur dioxide emission trends are reviewed in relation to sulfur dioxide air quality in the Los Angeles area. Emission fluctuations over the 19-year period from 1956 through 1974 are explained in terms of emission control policy changes. Simple statistical tests indicate that measured SO_2 air quality levels at Long Beach and downtown Los Angeles track changes in emission strength at nearby sources and from sources with low effective stack height.

Atmospheric oxidation of SO_2 to form particulate sulfates is discussed. Sulfate air quality measurements at Los Angeles show a broad summer seasonal peak in all years of record, with isolated periods of very high sulfate concentration in some winters of record. The geographic distribution of long term average sulfate concentrations is examined and found to be rather uniform across existing monitoring stations in the Los Angeles Basin. Fluctuations in measured sulfate values from day to day are shown to track changes in inversion height, relative humidity, total suspended particulate levels, and ozone concentrations. From these relationships, it is suggested that day-to-day fluctuations in sulfate concentration are driven mainly by changes in SO_2 to sulfate reaction rate and by changes in the effective mixing volume of the air basin.

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Introduction

When the smog problem in the Los Angeles Basin was first investigated, attention was focused on sulfur oxides emissions from industrial sources. Most of these emissions to the atmosphere were in the form of sulfur dioxide gas, which is known to be a mild respiratory irritant at elevated concentrations. Additional atmospheric measurements also identified particulate sulfur compounds, often referred to in the early literature as sulfuric acid mist or its gaseous precursor, sulfur trioxide. These particulate sulfur compounds were initially believed to be responsible for "thirty to sixty percent of the total reduction in visibility" at Los Angeles (L.A. APCD, 1950).

As the sulfur dioxide emission control program succeeded in reducing ambient SO_2 concentrations, and as the extremely complex chemical nature of photochemical smog became better understood, public attention was directed at the control of emissions from the automobile which dominated other aspects of local air quality. Recently, two things have happened which suggest that current control strategies for sulfur oxides should be reviewed.

The first of these is a projected increase in Basin-wide sulfur dioxide emissions due to curtailment of natural gas deliveries to Southern California. Figure 1 shows the Pacific Lighting Corporation's (1975) estimated gas supplies from existing sources in contrast to projected requests for service at current prices. It has been estimated by the Los Angeles Air Pollution Control District that substitution of sulfur-bearing fuel oil for natural gas combustion over the next few years will increase SO_2 emissions in Los Angeles County from a 1970 low of 250 tons per day to a level of about 450 tons per day by 1979 (see Appendix I). For the entire South Coast Air Basin, the California Air Resources Board has estimated that SO_2 emissions will increase from a 1973 level of 515 tons per day to a level of between 720 and 920 tons per day by 1983 (CARB, 1975). Since these emission rates are similar

PACIFIC LIGHTING CORPORATION
NATURAL GAS SUPPLY VS. EXPECTED REQUESTS FOR SERVICE AT CURRENT PRICES

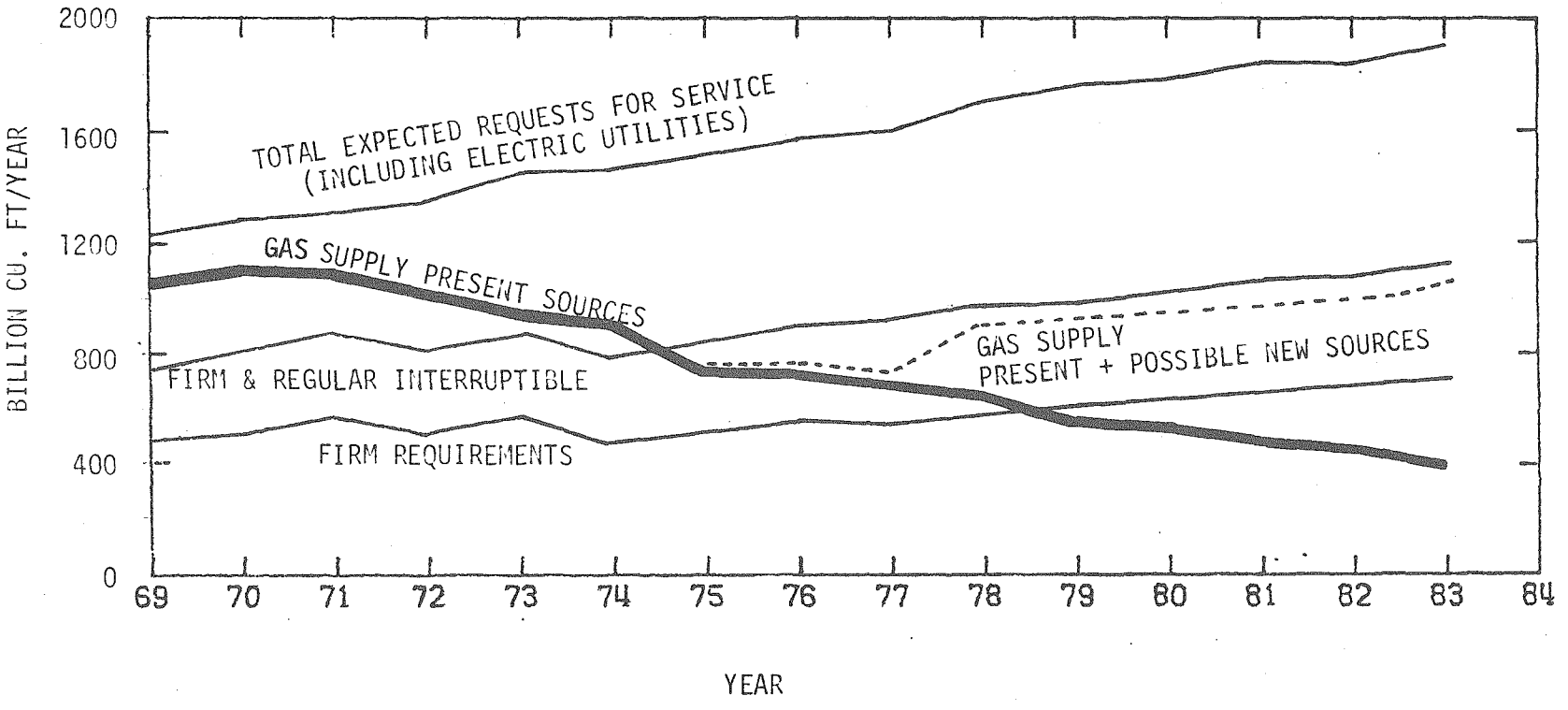


FIGURE 1

to those of the late 1950's, this paper will first review past SO_2 emission and air quality trends in the hope that they will shed considerable light on expected future SO_2 air quality.

The second focus for review of the status of sulfur oxide air quality control is a rekindling of interest in the role of particulate sulfates in the atmosphere. Sulfates contribute to visibility reduction (White and Roberts, 1975) and are of current public health concern (National Research Council, 1975). In the second part of this paper, we will review recent sulfate air quality trends in the Los Angeles Basin and the atmospheric circumstances associated with sulfate formation and dispersion.

Sulfur Dioxide Emission Trends

A brief historical account (L.A. APCD, 1975) of past sulfur oxides management policy in the Los Angeles area will help put many of these issues into perspective. When the nature of the Los Angeles smog problem was first investigated in the late 1940's, considerable attention was focused on the need for sulfur dioxide emission controls. In 1947, prior to the imposition of any discharge limitations, sulfur dioxide emissions in Los Angeles County totaled about 680 tons per day, distributed amongst source categories as shown in Table I (Lemke, et al., 1969).

In 1947, the Los Angeles Air Pollution Control District adopted Rule 53 which limited sulfur compounds in exhaust gases to 0.2 percent by volume (calculated as SO_2). By 1958, enforcement of this regulation had resulted in a lowering of total SO_2 emissions within the County to a level of 453 tons per day. The bulk of this initial reduction was achieved by removal of hydrogen sulfide from refinery gases prior to their combustion. Other refinery process operations were also affected. As shown in Figure 2, non-fuel-burning refinery process SO_2 emissions dropped sharply in 1957 and have remained relatively unchanged thereafter over the past eighteen years. Changes in sulfur dioxide emissions from refinery fuel burning are reflected in the "other" category of Figure 3.[1]

[1]Data on emission trends and projections used in Figures 2 through 4 were provided by the L.A. APCD as detailed in Appendix I. Missing data were estimated by linear interpolation. The "other" SO_2 emission category defined by the L.A. APCD in Appendix I is dominated by industrial, commercial, and transportation fuel burning, and thus was graphed together with utility fuel combustion in Figure 3.

TABLE I

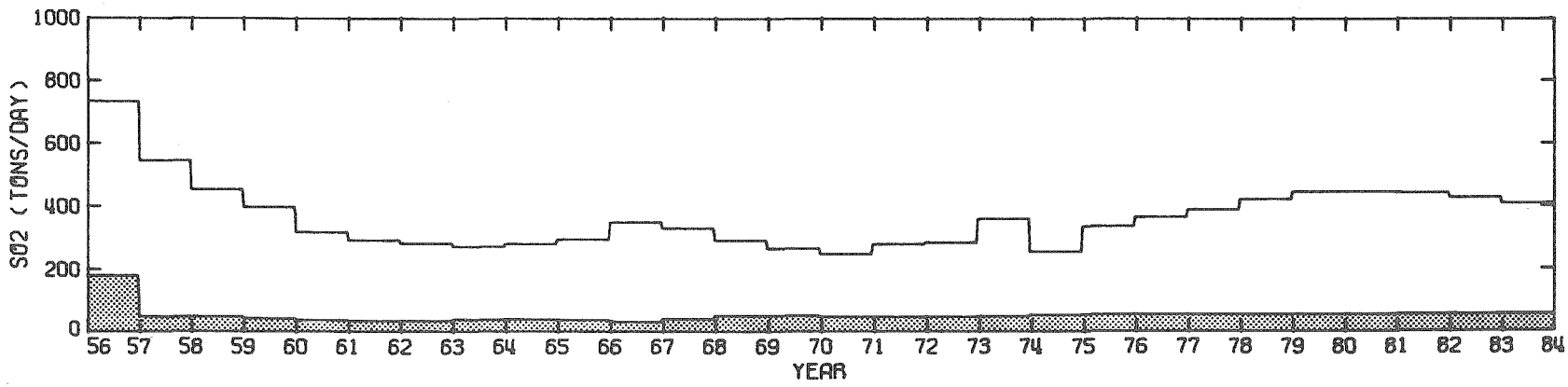
Sulfur Dioxide Emissions in Los Angeles County for 1947
(Prior to Initial Emission Control Regulations)

Source Class	SO_2 Emission Rate (Tons/Day)
(1) Combustion of Fuels Including: utility boilers refinery fuel industrial fuel	575
(2) Refinery Processes Operations	30
(3) Motor Vehicles	40
(4) Remaining Sources Including chemical plants	35
TOTAL	680

Note: Emission values are taken from a graph presented by Lemke, et al., 1969. This graph could be read no more closely than ±5 tons/day,

SØ2 EMISSIØNS FRØM REFINERY PRØCESS ØPERATIØNS (SHADED)

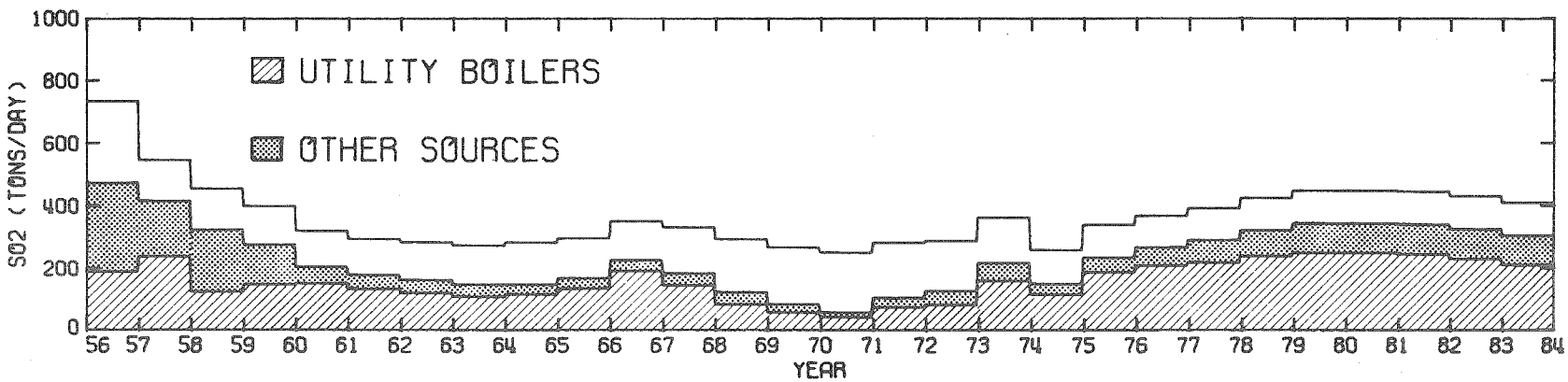
AND TØTAL SØ2 EMISSIØNS IN LA CØUNTY, WITH LAAPCD FUTURE PRØJECTIØN



Reflects all SO_2 emissions from refinery processes except for fuel burning and sulfur recovery operations. Includes activities such as catalyst regeneration, waste water treatment, distillation losses, plus asphalt and by-product processing.

FIGURE 2

SO2 EMISSIONS FROM FUEL BURNING (SHADED) AND TOTAL SO2 EMISSIONS IN LA COUNTY WITH LAAPCD FUTURE PROJECTION



The Other Sources category includes SO_2 emissions from fuel combustion by industrial, commercial, institutional, and commercial transportation sources, plus miscellaneous industrial process emissions.

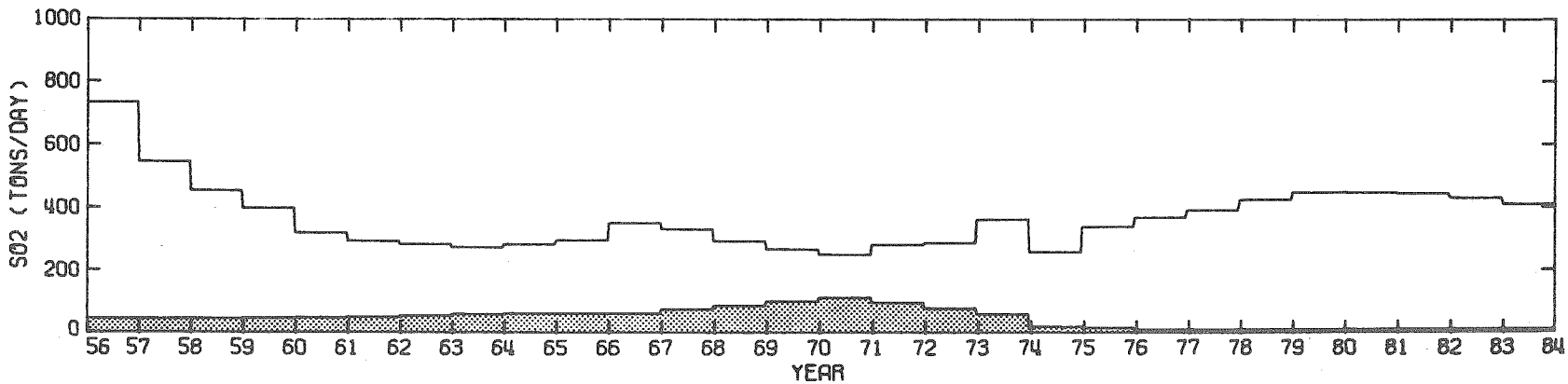
FIGURE 3

In 1958, Rule 62 was adopted by the L.A. APCD. The regulation prohibited the burning of any solid or liquid fuel containing over 0.5 percent sulfur by weight from May through November of the year, *provided that natural gas was otherwise available*. Rule 62 first went into effect in the summer of 1959. Referring to Figure 3, we note a steady drop in SO_2 emissions from fuel burning following adoption of Rule 62, reaching a relative minimum in about 1963.

In spite of continued restrictions on the sulfur content of fuel, expansion of electric generating capacity in the Basin caused an increase in total SO_2 emissions beginning in about 1963. In January of 1964, Rule 62 was amended (by adoption of Rule 62.1) to make the sulfur content of fuel provisions applicable year-round. A limited supply of natural gas during the winter months rendered that change ineffective at slowing the growth in total emissions. These increasing emissions from stationary source fuel burning were eventually reversed in the late 1960's by importation of low sulfur fuel oil from Indonesia and Alaska, and by increased deliveries of natural gas. By October of 1968, Rule 62 was again amended to prohibit the burning of high sulfur fuel oil, irrespective of natural gas supply conditions. Shortly thereafter, natural gas deliveries began to diminish, with attendant substitution of low sulfur fuel oil leading to the upward trend in SO_2 emissions from fuel burning projected for Los Angeles County in the decade of the 1970's in Figure 3.

Another long-term feature of the SO_2 emission inventory for Los Angeles County is the emergence and subsequent control of substantial pollutant emissions from chemical process industries. In order to reduce emissions from refinery operations, sulfur-bearing refinery gases were often transported to adjacent plants which recovered elemental sulfur or sulfuric acid from the refinery effluent. These sulfur recovery operations were not one hundred percent efficient, and in time became major SO_2 sources in their own right. By 1970, Figure 4 shows that chemical processes accounted for 115 tons per day of SO_2 emissions, or nearly half of the total SO_2 emission inventory at that time. In

SØ2 EMISSIONS FROM CHEMICAL PLANTS (SHADED) AND TØTAL SØ2 EMISSIONS IN LA COUNTY WITH LAAPCD FUTURE PRØJECTIØN



Includes sulfur recovery and sulfuric acid operations associated with petroleum refining.

FIGURE 4

1971, Rule 53 was amended (effective 1973) to repeal certain exemptions previously granted to scavenger plants and to limit effluent streams from these plants to not more than 500 ppm of sulfur compounds calculated as SO_2. A maximum emission rate of not more than 200 pounds per hour of sulfur-bearing gases calculated as SO_2 was also imposed at that time. Figure 4 clearly shows the effect of these regulations on 1974 and subsequent SO_2 emission rates.

Automotive exhaust contains sulfur oxides derived from trace amounts of sulfur initially present in gasoline. California gasolines have traditionally been higher in sulfur content than the national average (Bureau of Mines). As shown in Figure 5, SO_2 emissions from automobiles totaled about 35 tons per day in Los Angeles County in the mid 1950's. Increased sophistication of refining operations permitted a decline in the sulfur content of local gasolines in the following decade. In spite of progressive increases in vehicle miles traveled yearly, automotive SO_2 emissions in Los Angeles County declined, reaching a minimum of 23 tons per day in 1965. Since that time, increased gasoline consumption has returned sulfur dioxide emissions from automobiles to the vicinity of 30 tons per day. Although automotive SO_2 emissions represent only about 10 percent of the total SO_2 emission inventory, they are important to an understanding of Los Angeles sulfur oxide air quality for at least two reasons. First, automotive emissions occur at ground level where atmospheric dispersion is least effective at diluting the effluent prior to reaching receptor populations (and local air monitoring stations). Secondly, there is a potential for conversion of auto exhaust SO_2 to sulfuric acid mist if the exhaust is passed over an oxidizing catalyst intended for hydrocarbon and carbon monoxide control.

Sulfur Dioxide Air Quality Trends

Sulfur dioxide emissions undergo atmospheric transport, dilution, and removal processes resulting in the SO_2 concentrations measured at receptor air monitoring stations. Figure 6 displays the seasonal trends

SO2 EMISSIONS FROM AUTOMOBILES (SHADED) AND TOTAL SO2 EMISSIONS IN LA COUNTY

WITH LAAPCD FUTURE PROJECTION

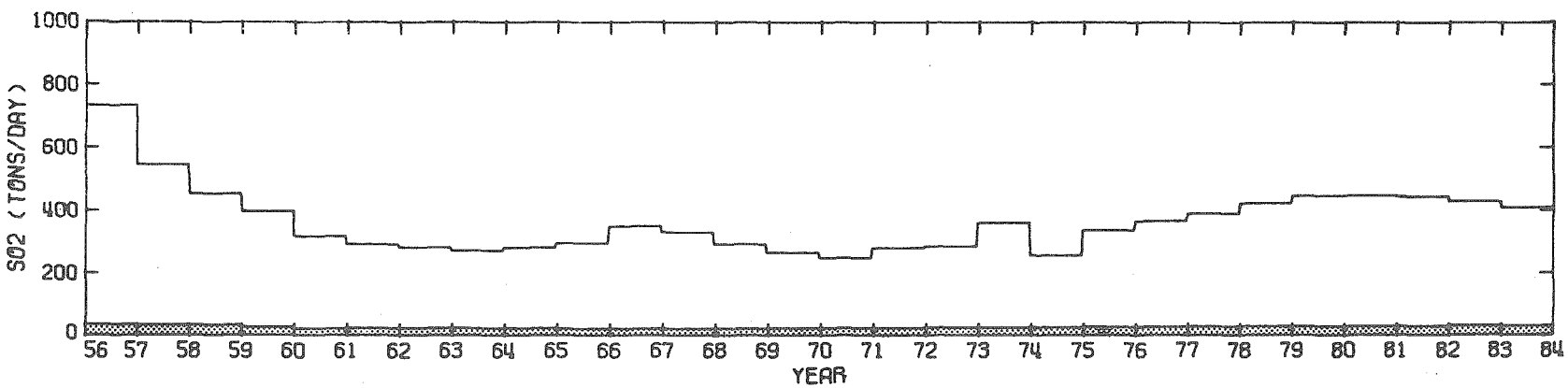
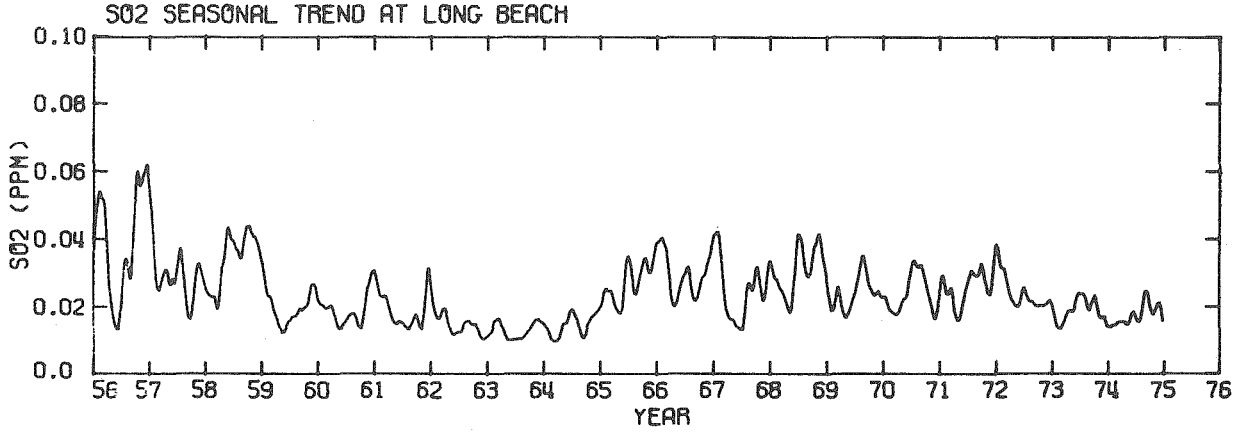


FIGURE 5


SO2 SEASONAL TREND AT LONG BEACH
0.10
0.08
0.06
0.04
0.02
0.0
SO2 (PPM)
56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76
YEAR

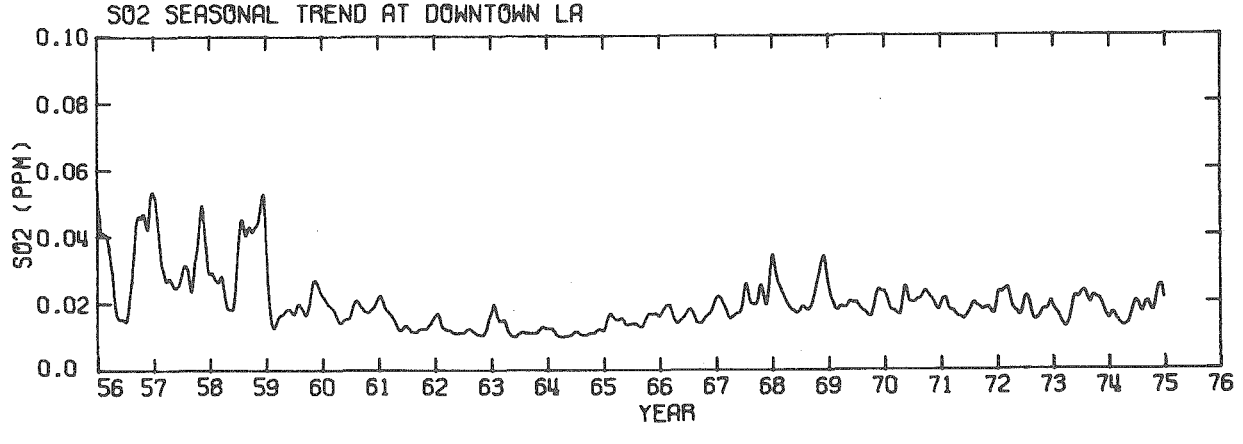

SO2 SEASONAL TREND AT DOWNTOWN LA
0.10
0.08
0.06
0.04
0.02
0.0
SO2 (PPM)
56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76
YEAR

FIGURE 6

in SO_2 measurements over the past two decades at two such monitoring stations: Long Beach and downtown Los Angeles. Long Beach is chosen because it represents a location in the vicinity of major SO_2 sources in the harbor area. On the other hand, downtown Los Angeles is a commercial center located about 15 miles inland from the major coastal point sources of SO_2.

These ambient air quality graphs were generated by passing the time sequence of the L.A. APCD's 24-hour average SO_2 readings over the period of interest through a linear digital filter.[2] The effect of this processing is to reveal long-term air quality trends by smoothing out fluctuations with frequency greater than four cycles per year, leaving the seasonal variations intact.

Referring to Figure 6, the following observations can be drawn. SO_2 air quality has improved since the mid 1950's at both Los Angeles and Long Beach. A sharp drop in SO_2 concentration occurred at both locations in 1959, at about the same time as the imposition of the initial controls on sulfur content of fuel oil. From 1959 to 1963, air quality improved slightly at both locations, reaching a relative minimum in 1963 at the same time as the 1963 relative minimum in SO_2 emissions. SO_2 levels then rose, accompanying the subsequent mid-1960's emission increases. Since 1970, SO_2 concentrations at downtown Los Angeles have remained relatively constant, while at Long Beach a declining trend is apparent over the period 1972 through 1974.

An Emissions-to-Air-Quality Relationship for SO_2 at Long Beach and Downtown Los Angeles

Given distinct trends in both emissions and air quality, a rather simple treatment can be shown to yield interesting observations about the air quality impact of emission control policies.

The linear rollback technique is often used to make "back of the envelope" air quality projections. It assumes that current air quality

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[2]The filter's characteristics are such that it returns the low frequency signal with zero gain, half power cutoff set to remove disturbances with period shorter than three months, and roll off at the half power point of 20 db per octave. For a discussion of digital filtering methods, see Bendat and Piersol, Chapter 9.2.

levels are proportional to current Basin-wide emission levels, and that ambient pollutant concentrations "can be scaled down in direct proportion to emission intensity until background air quality is achieved at zero emissions" (Seinfeld, 1975). This sort of approximation is likely to be true, however, only if the spatial distribution of emission sources remains unchanged, if the emission reductions are applied uniformly across all source classes, and if atmospheric chemical reactions do not introduce non-linear effects.

In practice, however, even if source locations remain unchanged, it is usually less expensive, technically less risky, or administratively more expeditious to control emissions from different source classes to different degrees of stringency or to prescribe different time schedules for completion of abatement activity. Basin-wide spatial homogeneity of emission reduction seldom is achieved in any real situation involving a stationary source emission problem. Instead, in this analysis, the assumption of uniform emission reduction across all source classes will be relaxed, and a "categorized" or "fitted" rollback model will be proposed.

The following assumptions are made:

(A) SO_2 air quality measured at a receptor site is a linear combination of contributions from a variety of source classes which will each be treated as a group for regulatory purposes.

(B) The spatial distribution of members of each source class remains unchanged over long periods of time.

(C) Emission changes experienced within each source class are distributed geographically in proportion to previous emission levels from that source class.

Then given observations on air quality for t time periods, plus emissions estimates for each of the n source classes, with $t > n$, one

can estimate the coefficients of the following categorized rollback air quality model by linear regression techniques:

$$(1) \qquad C_{jk} = \sum_{i=1}^{n} \beta_{ik} E_{ij} + \alpha + \varepsilon_j$$

where C_{jk} is the pollutant concentration at receptor site k during time period j;

E_{ij} is the emission rate from source class i during time period j;

β_{ik} is an undetermined emission-to-air-quality transfer coefficient from source class i to receptor site k;

α is an undetermined constant reflecting background air quality levels for the pollutant of interest (plus the effect of certain systematic measurement errors, if any);

ε_j is the residual for time period j resulting from the least squares fit.

Table II shows the results of applying the model of Equation (1) to the SO_2 emissions-to-air-quality relationships at Los Angeles and Long Beach. The annual average of SO_2 air quality measurements for each of the 19 years from 1956 through 1974 at these two locations was used in these computations in conjunction with 19 years of emission data from Figures 2 through 5 for the five source classes defined in Appendix I: power plants, refinery process operations, chemical plants, miscellaneous sources (including industrial fuel burning), and automobiles. All computations were performed using the step-wise ordinary least squares regression package of the MAGIC data handling program maintained on the Caltech IBM 370/158 computer by R. C. Y. Koh.

The fit between observed and computed air quality levels at downtown Los Angeles is particularly good. The correlation coefficient between observation and model estimate is 0.90. A principal SO_2 source at downtown Los Angeles over the 19-year period is identified as the automobile,

TABLE II

MODEL ESTIMATED:

$$SO_{2_j} = \beta_{auto} \cdot \left[\text{auto } SO_2 \text{ emissions}\right]_j + \beta_{chemical} \cdot \left[\text{chemical plant } SO_2 \text{ emissions}\right]_j + \beta_{\substack{refinery \\ process}} \cdot \left[\text{refinery process } SO_2 \text{ emissions}\right]_j + \beta_{utility} \cdot \left[\text{utility fuel } SO_2 \text{ emissions}\right]_j + \beta_{other} \cdot \left[\text{other } SO_2 \text{ emissions (mostly fuel combustion)}\right]_j + \alpha + \epsilon_j$$

LOCATION	NUMBER OF YEARS OF OBSERVATION (COMMENTS)	SO_2 AVERAGE (SO_2 VARIANCE)	COEFFICIENTS (t test) β_{auto}	$\beta_{chemical}$	$\beta_{refinery\ process}$	$\beta_{utility}$	β_{other}	α	CORRELATION COEFFICIENT (Variance of Residual)
Los Angeles	19 (all variables entered)	0.020 (4.52×10^{-5})	1.06×10^{-3} (3.33)	1.05×10^{-4} (3.03)	-2.70×10^{-5} (0.92) ns	1.22×10^{-5} (0.66) ns	5.14×10^{-5} (2.31)	-0.020	0.90 (6.24×10^{-6})
Los Angeles	19 (intercept, α, supressed)	0.020 (4.52×10^{-5})	1.47×10^{-4} (3.11)	3.43×10^{-5} (2.1)	-4.21×10^{-5} (1.33) ns	-9.53×10^{-6} (0.57) ns	8.55×10^{-5} (5.01)	0.0 (fixed)	
Long Beach	19 (all variables entered)	0.024 (4.75×10^{-5})	2.01×10^{-4} (0.39) ns	1.82×10^{-4} (3.22)	2.89×10^{-5} (0.60) ns	3.57×10^{-5} (1.19) ns	5.91×10^{-5} (1.63) *	-0.004 ns	0.72 (1.66×10^{-5})
Long Beach	19 (intercept, α, supressed)	0.024 (4.75×10^{-5})	8.40×10^{-5} (0.39) ns	1.76×10^{-4} (3.48)	2.60×10^{-5} (0.56) ns	3.15×10^{-5} (1.27) ns	6.57×10^{-5} (2.63)	0.0 (fixed)	

Notes:

(a) UNITS: SO_2 in ppm; β's in ppm/ton SO_2 per day; α in ppm

(b) All coefficients significantly different from zero with greater than 95% confidence unless otherwise indicated:

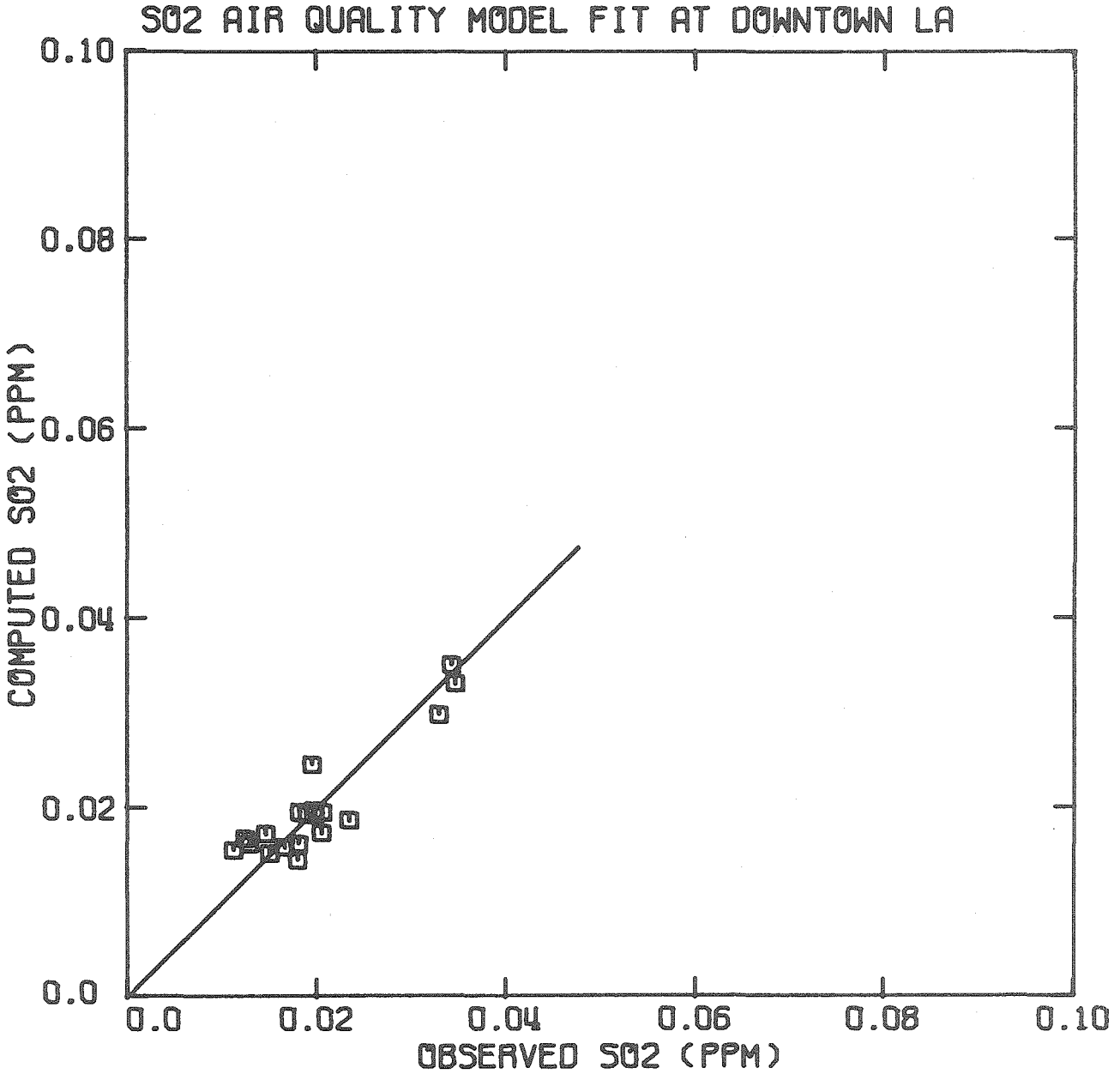
ns - not significantly different from zero at 95% confidence level

* - not significantly different from zero at 95% confidence level, but coefficient is of expected sign and significantly greater than zero above the 90% confidence level in a one-tailed test of the null hypothesis in which negative coefficients are considered physically impossible.

followed in importance by chemical plants and industrial and commerical fuel burning. Refinery fuel-burning emissions, which are considerable, are included in this miscellaneous fuel-burning category. Emissions-to-air-quality coefficients for these three source classes are all of positive sign and significantly different from zero with greater than 95 percent confidence. Emissions-to-air-quality coefficients at downtown Los Angeles for power plants and refinery process operations would not pass a conventional significance test. This could be due either to minor ground level SO_2 impact of these sources or to violation of the spatial homogeneity assumptions of our model. Power plant emission changes due to generating capacity expansion may well be inadequately modeled by considering emissions within Los Angeles County alone. The inability to locate an obvious major source ground level SO_2 impact at downtown Los Angeles of course says nothing about whether such impact occurs elsewhere.

The negative background estimate, α, is statistically significant but physically unacceptable. Therefore, the intercept was suppressed and the regression analysis was repeated. The results are substantially the same as before, except that a stronger dependence is indicated on the miscellaneous industrial processes and non-utility fuel-burning emissions which dominate the "other" category of the emissions classification scheme. Even with the intercept suppressed, correspondence between observed and computed SO_2 air quality levels is good, as shown in Figure 7.

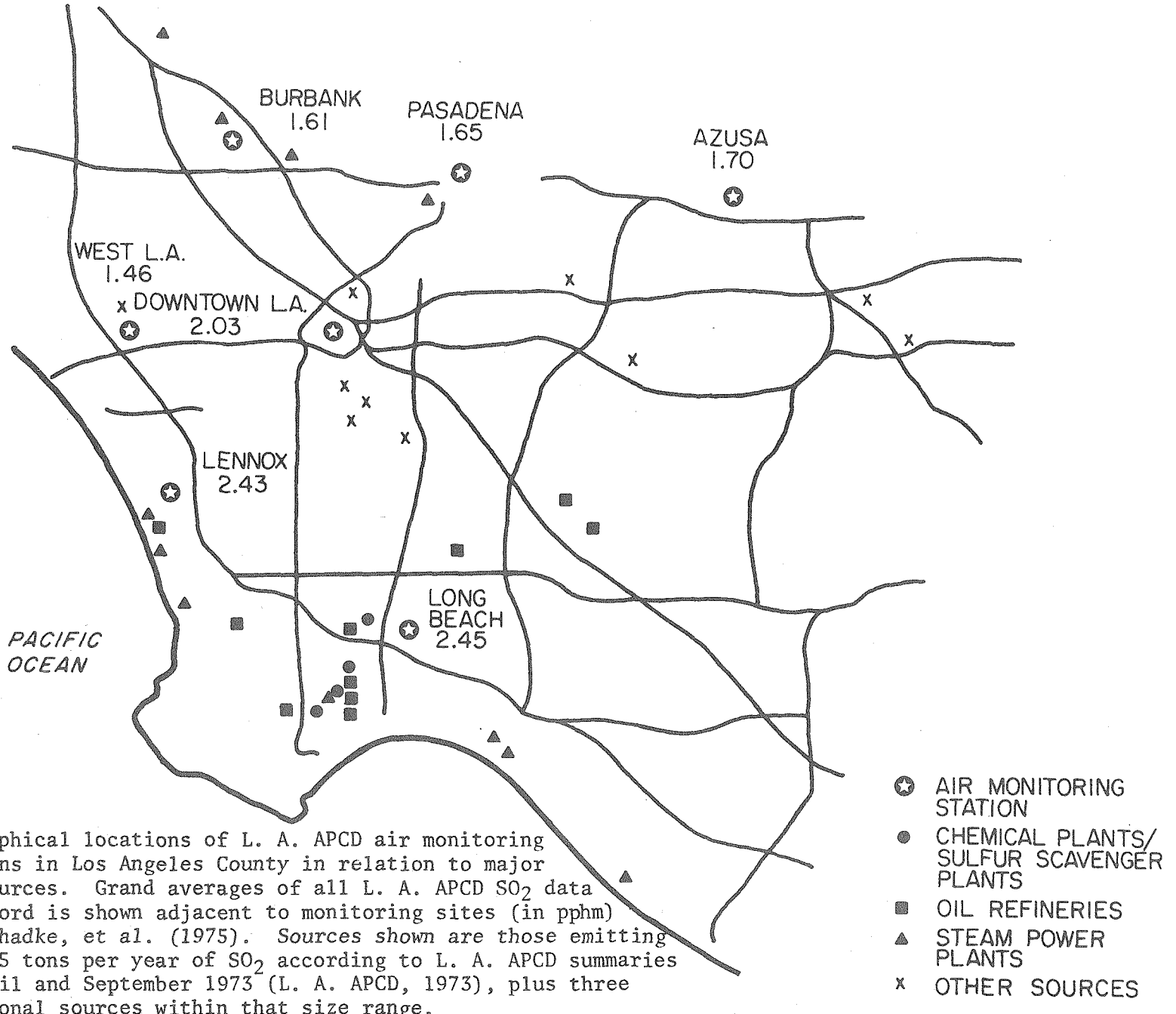
Model results at Long Beach are qualitatively similar. The principal contributor to SO_2 air quality fluctuations at the Long Beach air monitoring station is identified as the chemical process industry. Referring to Figure 8, we note that this is not at all surprising. Three of the closest sources to the Long Beach monitoring station are chemical plants, one of which was the largest SO_2 emitter (by a factor of two) within Los Angeles County as recently as the early 1970's. The



SO_2 concentrations shown are annual arithmetic means.

Intercept, α, of Eq. (1) is suppressed.

FIGURE 7



Geographical locations of L. A. APCD air monitoring stations in Los Angeles County in relation to major SO_2 sources. Grand averages of all L. A. APCD SO_2 data of record is shown adjacent to monitoring sites (in pphm) from Phadke, *et al.* (1975). *Sources shown are those emitting* over 25 tons per year of SO_2 according to L. A. APCD summaries of April and September 1973 (L. A. APCD, 1973), plus three additional sources within that size range.

FIGURE 8

next strongest influence at the Long Beach station is industrial fuel-burning emissions. The intercept, α, fitted at Long Beach is insignificantly different from zero, indicating the presence of measurable quantities of SO_2 at most times.

The conclusions drawn form these two regression model applications support the results of numerous conventional air quality diffusion modeling studies. As is usually found to be the case for a pollutant emitted directly from a source (as opposed to those pollutants formed by chemical reaction in the atmosphere), it is the sources with low effective stack height and those geographically close that dominate air quality at a receptor site.

This analysis was performed at only two locations to illustrate the technique involved. A more complete picture of SO_2 air quality can and should be obtained by study of air quality response to past emission changes at the remaining monitoring stations in the air basin, as well as by tracer studies and diffusion modeling in which the fate of pollutant emissions from elevated sources can be explicitly handled.

Los Angeles Sulfate Air Quality

In spite of the projected increases in SO_2 emissions, SO_2 levels in the Los Angeles area will probably still be considered low by national standards in future years. Unfortunately, the questions currently being asked about sulfur oxides air quality management are more complex than this.

Sulfur dioxide gas has been shown to undergo atmospheric oxidation to form suspended particulate sulfates. These sulfate particles tend to accumulate in a size range around 0.5 microns in diameter (Roberts, 1975). Particles of this size are extremely effective scatterers of light (Middleton, 1952) and are also capable of deep penetration into the lung (Task Group, 1966). Recent studies indicate that sulfates may be responsible for about half of the visibility reduction experienced

at downtown Los Angeles (White and Roberts, 1975). In addition, there is a body of toxicological (Amdur, 1973) and epidemiological evidence (Benson, et al., 1974) suggesting that sulfate particulates are much more irritating to the respiratory system per unit mass concentration than an equivalent amount of sulfur present as SO_2 alone. Sulfate air pollutants are thought to play an important role in the acidification of rain water (Committee on Mineral Resources and the Environment, 1975) and can be associated with chemical attack on materials (Middleton, et al., 1970).

It has been recognized since the early 1950's that the Los Angeles atmosphere exhibited sulfate concentrations comparable to those of cities in the industrial northeastern United States despite the fact that sulfur dioxide emissions in Southern California are modest by comparison. At the conclusion of an extensive aerometric survey of the Los Angeles area (Renzetti, et al., 1955), the question was posed, "Why are the sulfate and nitrate concentrations in the particulate loading in smog higher in Los Angeles than in other cities?" Twenty years later that question is only partially answered. In a recent position paper (EPA, 1975), the U.S. Environmental Protection Agency stated that a national regulatory strategy for sulfate control would not be proposed for at least three years due to a lack of clear understanding of several fundamental aspects of the sulfate pollution syndrome. More complete information is wanted on atmospheric sulfate concentrations, health and welfare aspects, and emission control technology. Perhaps some of these questions can be answered for the case of Los Angeles by analysis of the extensive air monitoring data base accumulated in past years.

Sulfate Air Quality Trends

Total suspended particulate matter samples have been collected by the L.A. APCD by high volume sampling on a regular basis since August 1965. The sampling period is 24 hours in duration. Samples are collected on glass fiber filters from which water-soluble sulfates are determined by the turbidimetric method. From August 1965 through August 1970, samples

were taken from 8:00 a.m. to 8:00 a.m. at intervals ranging from weekly to twice weekly to every fifth day. From September 1970 through the end of 1974, samples were taken from midnight to midnight at least at five-day intervals, with a strict five-day sampling schedule prevailing since July 1971. Sulfate air quality trends observed at downtown Los Angeles during the past decade are shown in Figure 9. As was the case with our previous treatment of SO_2 air quality, the raw data has been smoothed in order to expose seasonal trends. Recent data taken since July 1971 has been processed to remove fluctuations with period shorter than three months; the effective filtering applied to data taken prior to July 1971 is more difficult to interpret due to the unequal spacing of the observations.

It is apparent from Figure 9 that measured sulfate levels at downtown Los Angeles have risen over the past decade, reaching a relative peak in 1973. A small decline followed in 1974. Both the annual mean and upper bound of seasonal maxima follow this trend. There is a broad summer seasonal peak in sulfate levels apparent in most years of record. A winter-time peak is also apparent, but its magnitude varies greatly from year to year. In the winters of 1972-73 and 1973-74, for example, the winter peak was very small and confined to a few weeks around the first of the year, while in the winters of 1970-71 and 1971-72 the winter peak was characterized by isolated days of very high sulfate levels which led to elevated annual averages for those years.

A rather striking feature of sulfate air quality in the Los Angeles Basin is its spatial uniformity. Figures 10 and 11 show the relationship between sulfate levels measured at Lennox, downtown Los Angeles, and Pasadena on the same days during the years 1971 through 1973. These three monitoring sites lie approximately along a resultant sea breeze wind trajectory stretching from a major SO_2 source area at the coast through the central business district and into inland valleys beyond, as shown by comparing Figure 8 with Figure 12 (De Marrais, et al., 1965).

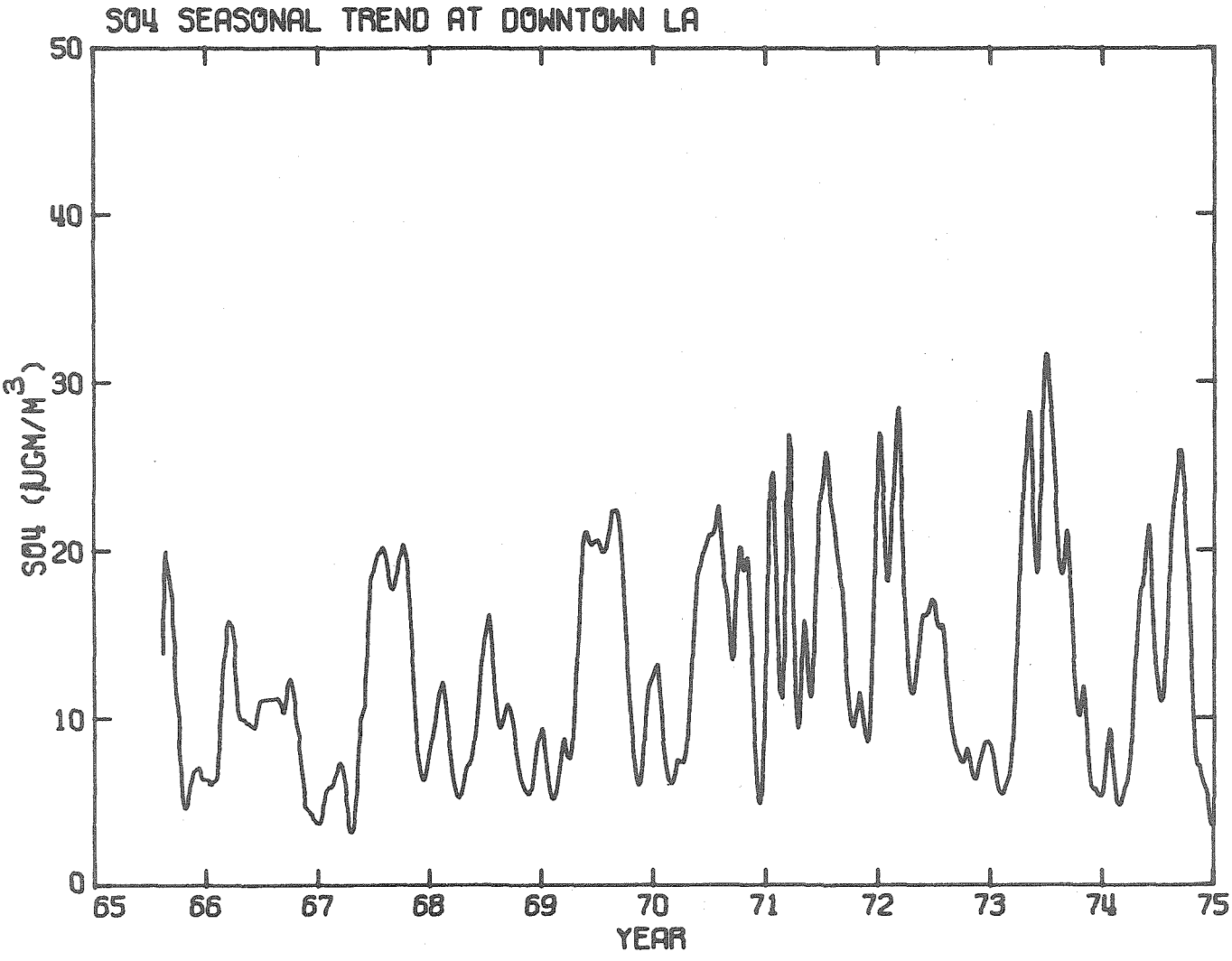

SO4 SEASONAL TREND AT DOWNTOWN LA
50
40
30
20
10
0
SO4 (μGM/M3)
65
66
67
68
69
70
71
72
73
74
75
YEAR

FIGURE 9

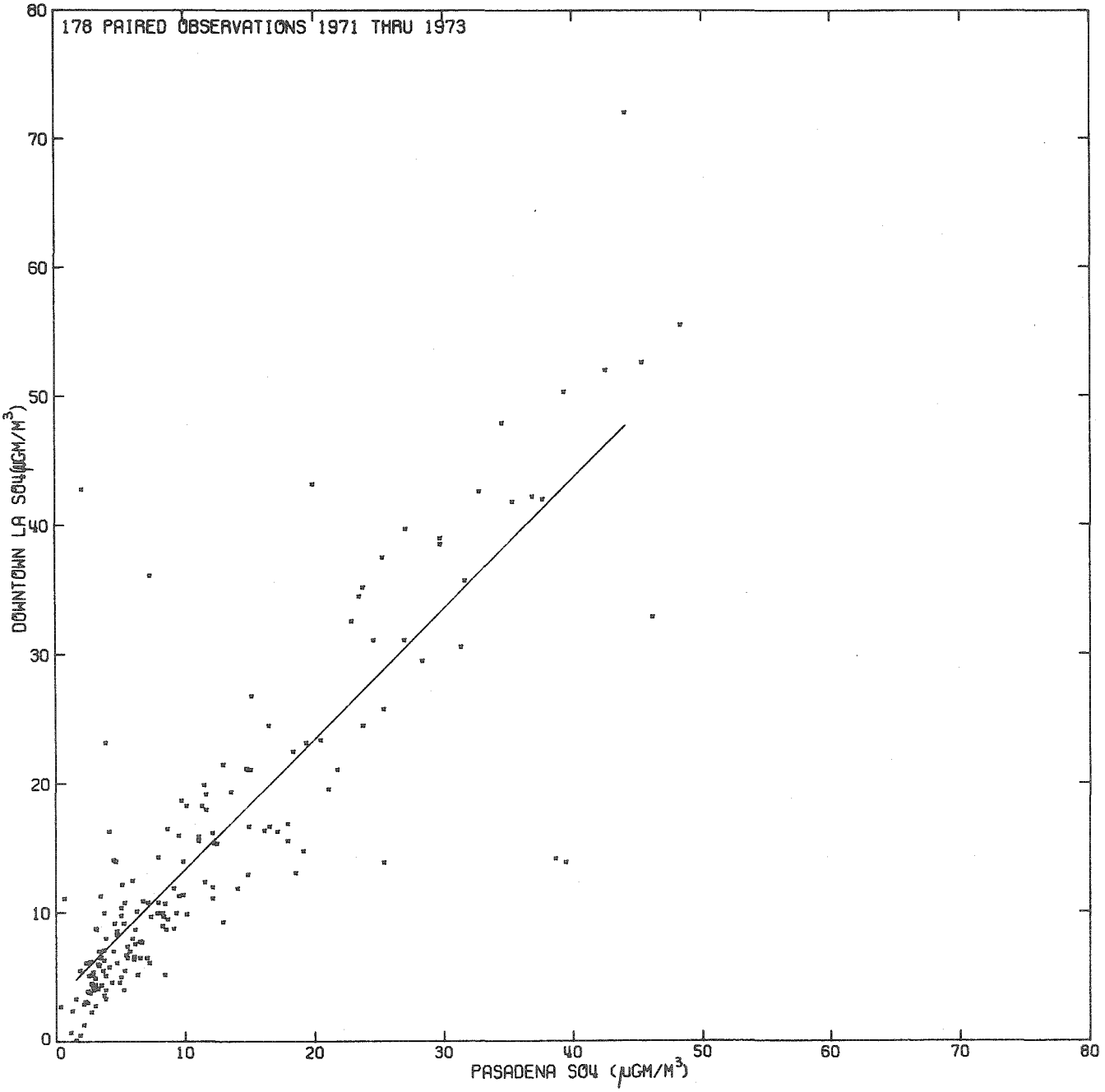

178 PAIRED OBSERVATIONS 1971 THRU 1973
DOWNTOWN LA SO4 (μGM/M3)
PASADENA SO4 (μGM/M3)
0
10
20
30
40
50
60
70
80

FIGURE 10

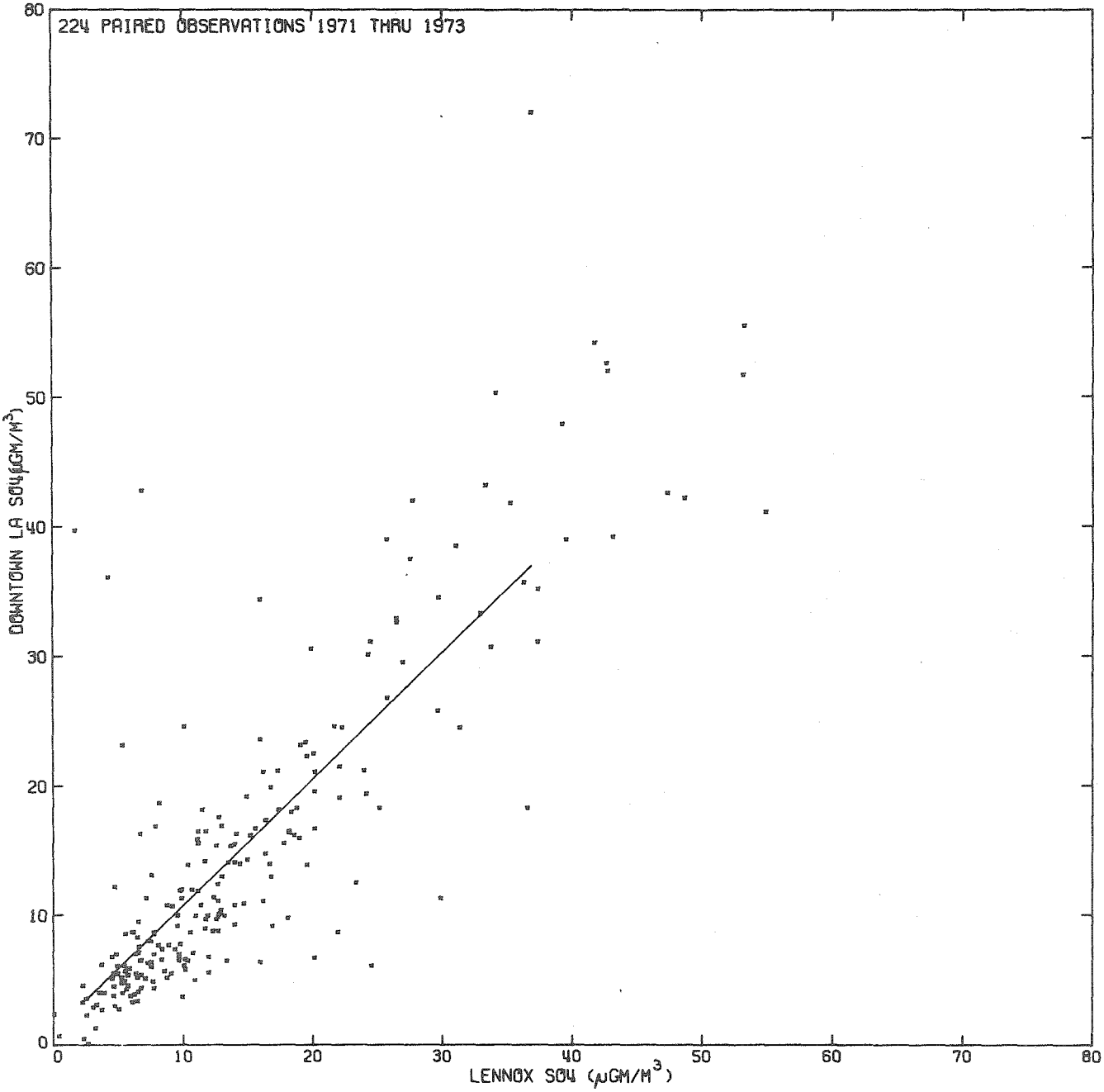
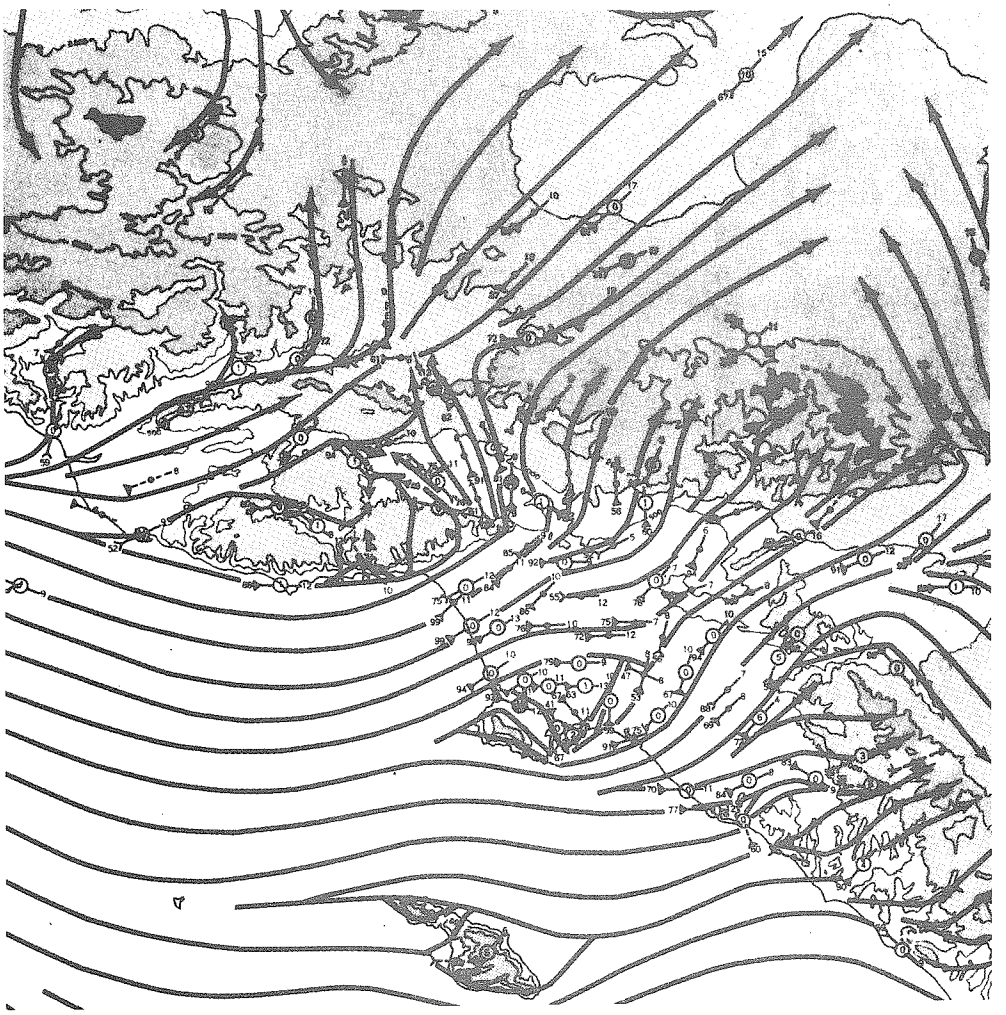

224 PAIRED OBSERVATIONS 1971 THRU 1973
DOWNTOWN LA SO4(μGM/M3)
LENNOX SO4 (μGM/M3)
0
10
20
30
40
50
60
70
80

FIGURE 11



WIND PATTERN CHART FOR JULY, 1200-1800 PST

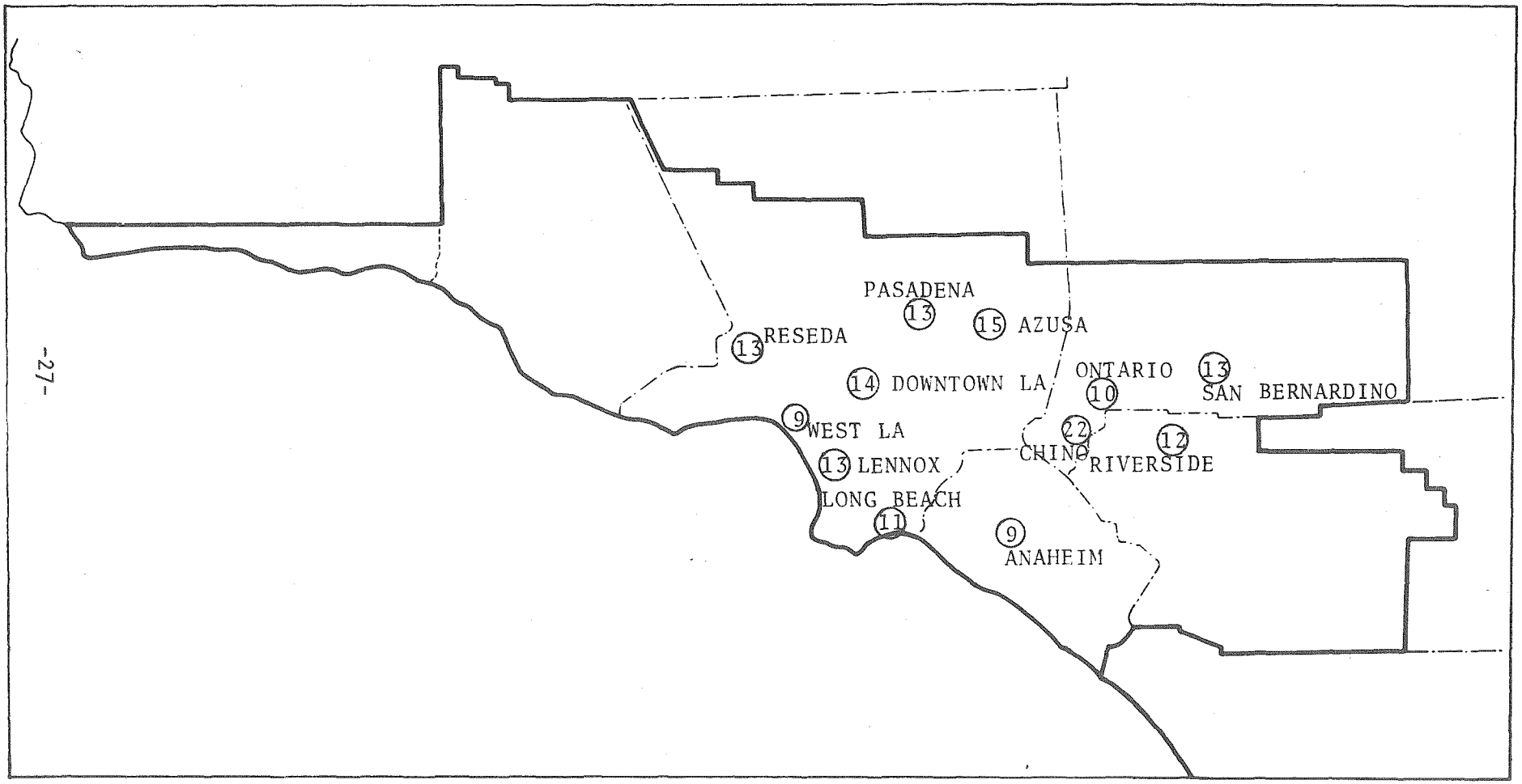
FIGURE 12

Sulfate values are approximately the same at all three locations on the same day, as shown by the unit slope and near zero intercept of the regression lines describing the best fit relationship between sulfate values at pairs of stations. This near equality of daily sulfate values at widely separated locations results in long-term mean sulfate concentrations of the same magnitude over most portions of the Basin, as shown in Figure 13 (Trijonis, et al., 1975).

This uniformity of long-term sulfate levels is in marked contrast to the highly localized nature of the major sources of precursor sulfur dioxide. For a conserved or slowly decaying pollutant emitted from coastal point sources, one expects pollutant concentration to drop greatly with distance downwind as atmospheric dispersion and removal processes come into effect. Sulfur dioxide concentrations do decline, as expected, with distance inland from the coast. The contrasting constant sulfate levels with distance inland from major sulfur oxide sources is probably explained by a competition between dispersion which tends to lower pollutant concentration and additional gas-to-particle conversion involving SO_2 which tends to build up sulfate concentrations. An alternative possibility is that sulfate concentrations accumulate aloft near the coast during late night and early morning stagnation periods. This well-aged aerosol might then be swept across the Basin during the day by the advancing sea breeze front, contributing roughly equal amounts of sulfate to successive air monitoring stations in passing.

The relative importance of various SO_2 to sulfate conversion mechanisms is poorly understood at present. SO_2 oxidation rates have been measured in the Los Angeles atmosphere and found to vary from one percent to 15 percent per hour under photochemically active, daylight sea breeze conditions (Roberts, 1975). At least three general classes of chemical reactions could oxidize SO_2 at rates fast enough to account for observed sulfate levels. These possibilities include (National Research Council, 1975):

THE SPATIAL DISTRIBUTION OF ARITHMETIC AVERAGE SULFATE AIR QUALITY
IN THE LOS ANGELES AREA
JULY 1971 THROUGH JUNE 1973



ALL VALUES IN $\mu GM/M^3$ AS $SO_4^=$ (from Trijonis, et al. (1975)).

FIGURE 13

1. Gas-phase oxidation of SO_2 by free radicals generated in Los Angeles photochemical smog;

2. Absorption of SO_2 by aqueous particles in the atmosphere, followed by catalytic oxidation in the liquid phase;

3. Surface adsorption of SO_2 by carbonaceous or metal oxide particles, followed by oxidation to sulfate.

At one time or another during the year, each of these reaction types may be important to explaining observed sulfate levels.

Fluctuations in sulfate concentrations from day to day are quite large. An empirical analysis of downtown Los Angeles air monitoring data was conducted to see if these day-to-day fluctuations in sulfate level at downtown Los Angeles could be shown to depend on fluctuations in meteorological dispersion or on factors affecting SO_2 to sulfate conversion rates. Meteorological dispersion indicators studied include early morning and afternoon inversion heights plus daily average wind speed, solar radiation intensity, and temperature. While changes in gas-phase free radical reactions are unobservable from conventional air monitoring data, there are data on possible indicators of the intensity of daily photochemical smog activity, including ozone concentrations, NO_2, and hydrocarbon level. Roberts (1975) showed that knowledge of ambient ozone levels improves the estimation of SO_2 oxidation rates in the Los Angeles atmosphere. If oxidation of SO_2 were occurring in the liquid phase on hydrated particles, then ambient relative humidity and suspended particulate concentrations would be important (along with such factors as ammonia concentration and catalytic metals levels, for which we do not have complete air monitoring data).

Data for over six hundred days of observation on air quality parameters and meteorological variables were reviewed, and 342 rainless days with a complete set of observations on all variables of interest were located.[3] This data set was matched to a step-wise regression model

[3] A statistical description of the explanatory variables used is given in Appendix II.

to determine which other atmospheric circumstances most closely track fluctuations in sulfate levels. Fluctuations in atmospheric variables generally have multiplicative effects on pollutant levels. For instance, halving the inversion height while doubling the reaction rate would quadruple expected sulfate concentrations, all other factors remaining equal. For this reason, our regression model was specified in multiplicative or log-linear form.

Results of these correlation studies are presented in Tables III and IV for the entire data base of record and for those samples taken since the change in sampling schedule of September 1970. Sulfate concentrations appear to be strongly inversely proportional to changes in afternoon inversion height. Sulfate concentration is found to be strongly dependent on daily relative humidity (RH) levels. This dependence on relative humidity is consistent with the observation of numerous investigators that a variety of sulfate formation mechanisms accelerate at high humidity. Knowledge of total suspended particulate matter (TSP) concentration provides a significant improvement in model fit. This is interesting because the grouping $TSP \cdot (1\text{-}RH)^{-1}$ for a hygroscopic aerosol would provide a term very roughly proportional to the volume of liquid water available in the atmosphere at a given time.[4] Further improvement in model fit is provided by the inclusion of daily average ozone concentration.

Beyond this point, improvements in model fit are provided mainly by attempts to better estimate the effects of the above phenomena through inclusion of ozone peak data, for example, rather than by entry of new explanatory variables. It is significant that changes in scalar average wind speed seem to bear little relation to sulfate concentrations. For primary pollutants linked to ground level area source emissions, such

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[4]Neiburger and Wurtele's (1949) discussion of water uptake by hygroscopic atmospheric particles develops the approximation that particle radius is roughly proportional to [particle solute mass/$(1\text{-}RH)$]$^{1/3}$. Particle volume is thus proportional to solute mass times $(1\text{-}RH)^{-1}$. If TSP is proportional to soluble particulate matter and the relative size distribution of dry solute mass per particle is preserved from day to day, then the above approximation follows.

TABLE III

Stepwise Regression of Log $SO_4^=$ on Logs of Other Pollutant and Meteorological Variables at Downtown Los Angeles

(For Description of Data Base, See Appendix II)

RESULTS: September 1970-1974 — 186 Days of Observation

First 5 Steps		Multiple Correlation Coefficient
STEP 1	$SO_4^= \propto \frac{1}{(1-RH)^{1.24}}$	0.66
STEP 2	$SO_4^= \propto \frac{(TSP)^{0.86}}{(1-RH)^{1.31}}$	0.78
STEP 3	$SO_4^= \propto \frac{(TSP)^{0.82}(Avg\ O3)^{0.44}}{(1-RH)^{1.28}}$	0.82
STEP 4	$SO_4^= \propto \frac{(TSP)^{0.65}(Avg\ O3)^{0.37}}{(1-RH)^{1.13}(Inv\ Max)^{0.39}}$	0.83
STEP 5	$SO_4^= \propto \frac{(TSP)^{0.75}(Inv\ Base)^{0.11}(Avg\ O3)^{0.39}}{(1-RH)^{0.92}(Inv\ Max)^{0.46}}$	0.85

VARIABLE TYPE	SYMBOL	ESTIMATED EXPONENT AT STEP 5	STANDARD ERROR OF THAT ESTIMATE
Total suspended particulate	TSP	0.75	0.09
$(1-\frac{\text{relative humidity}}{100}\%)$	1-RH	-0.92	0.10
Afternoon inversion height	Inv Max	-0.46	0.10
Morning inversion base height	Inv Base	0.11	0.03
24 hour avg. oxidant	Avg. O3	0.39	0.07

TABLE IV

Stepwise Regression of Log $SO_4^=$ on Logs of Other Pollutant and Meteorological Variables at Downtown Los Angeles

(For Description of Data Base, See Appendix II)

RESULTS: 1965-1974 — 342 Days of Observation

First 8 Steps		Multiple Correlation Coefficient
STEP 1	$SO_4^= \propto \frac{1}{(\text{Inv Max})^{1.36}}$	0.60
STEP 2	$SO_4^= \propto \frac{1}{(1-RH)^{0.61}(\text{Inv Max})^{1.07}}$	0.65
STEP 3	$SO_4^= \propto \frac{(TSP)^{1.10}}{(1-RH)^{1.14}}$	0.66
STEP 4	$SO_4^= \propto \frac{(TSP)^{0.77}}{(1-RH)^{0.81}(\text{Inv Max})^{0.73}}$	0.70
STEP 5	$SO_4^= \propto \frac{(TSP)^{0.84}(\text{Inv Base})^{0.23}}{(\text{Inv Max})^{1.08}}$	0.71
STEP 6	$SO_4^= \propto \frac{(TSP)^{0.92}(\text{Inv Base})^{0.16}}{(1-RH)^{0.54}(\text{Inv Max})^{0.80}}$	0.73
STEP 7	$SO_4^= \propto \frac{(TSP)^{0.88}(\text{Inv Base})^{0.15}(\text{Avg O3})^{0.21}}{(1-RH)^{0.56}(\text{Inv Max})^{0.72}}$	0.74
STEP 8	$SO_4^= \propto \frac{(TSP)^{0.96}(\text{Inv Base})^{0.12}(\text{Avg O3})^{0.85}}{(1-RH)^{0.55}(\text{Inv Max})^{0.72}(\text{O3 Max})^{0.55}}$	0.75

VARIABLE TYPE	SYMBOL	ESTIMATED EXPONENT AT STEP 8	STANDARD ERROR OF THAT ESTIMATE
Total suspended particulate	TSP	0.95	0.11
$(1-\frac{\text{relative humidity}}{100}\%)$	(1-RH)	-0.55	0.10
Afternoon inversion height	Inv Max	-0.72	0.10
Morning inversion base height	Inv Base	0.12	0.03
24 hour avg. oxidant	Avg. O3	0.85	0.18
Daily instantaneous oxidant peak	O3 Max	-0.55	0.15

as total hydrocarbons or CO, wind speed determines initial atmospheric dilution. When nearby sources dominate air quality for these pollutants, then wind speed and measured pollutant concentration are significantly negatively correlated. For a secondary pollutant formed in the atmosphere, such as sulfate, extensive mixing occurs during pollutant formation. Initial dilution is thus less important to observed concentrations than is the volume of the reactor (inversion height) and speed of the reaction.

A second approach to understanding the circumstances associated with high sulfate levels in Los Angeles is more subjective, but perhaps as instructive. Due to the typical time lag of several months between sulfate sample collection and analysis, few accounts of sulfate air quality contain any mention of the observer's description of the way the weather "looked" on days of abnormally high sulfate values. Of particular interest is whether weather conditions were conducive to high photochemical smog levels which would imply a gas-phase SO_2 to sulfate conversion mechanism, or whether conditions were typical of a London fog-type situation in which liquid-phase oxidation of SO_2 predominates. The L.A. APCD sulfate data base was scanned to select all days of record for which 24-hour average sulfate levels exceeded 30 $\mu gm/m^3$ at downtown Los Angeles.[5] Sixty-two such days were found. The weather <u>forecast</u> printed for each day in the <u>Los Angeles Times</u> was then reviewed, and the question asked, "Was the word fog mentioned in the forecast for that day at locations within Los Angeles and Orange Counties?" Then the U.S. Weather Service data logs for each of these days at coastal airports were reviewed to see if fog was <u>observed</u> that day at those locations. Unfortunately, Weather Service fog observations are unavailable at downtown Los Angeles. Then, daily ozone concentrations at downtown Los Angeles were recorded for both the daily instantaneous peak and 24-hour average corresponding to the period of each sulfate sample. The results of this sulfate episode survey are shown in Table V.

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[5]If duplicate samples were available, they were averaged to obtain the daily values used.

TABLE V

Atmospheric Humidification and Ozone on Days With

30 $\mu gm/m^3$ $SO_4^=$ or Greater at Downtown Los Angeles

DATE			DOWNTOWN LOS ANGELES SULFATE ($\mu gm/m^3$)	WAS FOG MENTIONED IN WEATHER FORECAST?					WAS FOG OBSERVED?		APPROXIMATE 24 HOUR AVG RELATIVE HUMIDITY @LA	OZONE	
Month	Day(s)	Year		L. A.	Beaches	San Fernando Valley	San Gabriel Valley	Orange County	L. A. Airport	Long Beach Airport		24hr Avg	Inst Max (pphm)
8	19/20	65	34.0					b			90.0	4.6	15
3	28/29	66	33.2	"drizzles"	"drizzles"	"drizzles"	"drizzles"	b			b	4.5	12
9	27/28	67	30.6			Yes	Yes	Yes	T. Precip	b	81.5	3.5	15
10	10/11	67	33.5	Yes	Yes	Yes	Yes	Yes	Yes 2	Yes 2ce	72.4	5.8	24
10	25/26	67	34.6	Yes	Yes	Yes	Yes	Yes	Yes	Yes 2e	75.9	6.4	29
2	20/21	68	34.4	Yes	Yes	Yes	Yes	Yes	b	Yes g	85.0	1.6	5
7	17/18	68	47.2						Yes d	Yes f	81.7	6.8	22
1	8/9	69	39.4	Yes	Yes	Yes	Yes	Yes			77.7	1.5	3
3	19/20	69	43.2	Yes	Yes	Yes	Yes	Yes	b	b	60.3	3.9	17
5	21/22	69	45.7	Yes		Yes	Yes	Yes	T. Precip c		77.3	5.1	12
7	9/10	69	31.2			Yes	Yes	Yes	Yes		70.0	4.6	14
8	27/28	69	43.6			Yes	Yes	Yes	Yes e		77.9	7.0	21
9	24/25	69	41.6	Yes		Yes	Yes	Yes			78.5	b	b
1	21/22	70	44.5	Yes					Yes 2	Yes 2	89.6	1.3	3
3	25/26	70	30.4	Yes	Yes	Yes	Yes	Yes	T. Precip c		67.1	4.0	13
6	3/4	70	42.8	Yes	Yes	Yes a	Yes a	Yes	Yes e	Yes e	63.5	3.8	17
7	8/9	70	34.3								76.3	3.7	14
8	5/6	70	30.1	Yes		Yes	Yes	Yes	Yes c	Yes 2c	72.2	4.0	13
8	10/11	70	43.8	Yes				Yes	Yes 2	Yes 2e	64.2	4.8	17
9	2	70	33.0	Yes	Yes			Yes			75.7	6.0	21
10	5	70	38.6	Yes	Yes	Yes	Yes	Yes	T. Precip	T. Precip f	87.2	2.3	6
10	19	70	39.3	Yes	Yes						78.8	3.1	12
1	25	71	54.2	Yes		Yes	Yes	Yes	Yes	Yes	65.8	2.8	9
2	1	71	30.1		Yes			Yes		Yes 2	69.6	1.2	2
2	8	71	41.1	Yes	Yes	Yes	Yes	Yes	Yes	Yes 2	69.1	2.0	10
2	15	71	30.7	Yes		Yes	Yes	Yes	Yes e		71.9	1.8	5
3	22	71	39.2				Yes				71.0	b	b
3	24	71	51.7			"drizzle"	"drizzle"				73.3	1.9	6
5	12	71	39.0			Yes	Yes	Yes	Yes	Yes	84.5	1.9	9
7	7	71	43.2			Yes	Yes				72.4	3.8	13
7	22	71	47.9			"sprinkles"	"sprinkles"		T. Precip		76.1	3.6	12
8	21	71	31.1				Yes				70.0	3.7	12
9	15	71	32.6	Yes	Yes	Yes	Yes	Yes			67.9	1.1	4
11	9	71	39.7	Yes	Yes	Yes	Yes	Yes	Yes 2	Yes 2	66.9	3.2	9
1	8	72	34.5	Yes	Yes			Yes	Yes	Yes	79.6	1.1	3
1	18	72	38.5	Yes	Yes	Yes	Yes	Yes	Yes	Yes	82.3	1.2	3
1	23	72	41.8	Yes			Yes	Yes		Yes	83.0	1.3	4
2	17	72	35.2	Yes	Yes			Yes	Yes 2	Yes 2	73.5	2.0	7
3	8	72	32.9	"drizzles"	Yes	Yes	Yes	"drizzles"			84.5	2.6	7
3	13	72	55.5	Yes	"drizzles"	Yes	Yes	Yes	Yes		87.7	2.2	9
3	18	72	52.6	"drizzles"		"drizzle"	Yes	"drizzle"	Yes f		83.7	4.2	13
6	1	72	33.3						Yes f		80.0	5.5	21
8	5	72	34.4			Yes	Yes				60.9	4.2	13
4	12	73	37.5		Yes	Yes	Yes	Yes			78.1	3.6	12
4	27	73	50.3						Yes	Yes	78.6	2.0	8
5	12	73	42.0	Yes	Yes	Yes	Yes	Yes	"drizzle"	"drizzle"	80.0	3.4	8
5	17	73	72.0		Yes	Yes	Yes	Yes	Yes	"drizzle"	75.6	3.5	13
6	26	73	52.0	Yes	Yes	Yes	Yes	Yes	Yes	Yes	68.6	4.6	24
7	1	73	42.2				Yes				74.5	4.3	14
7	6	73	35.7			Yes	Yes			T. Precip	80.8	1.8	6
7	11	73	42.6			Yes	Yes				75.8	3.7	13
7	31	73	31.1			Yes	Yes		Yes f		75.9	3.7	12
8	5	73	30.6						T. Precip	T. Precip	85.3	4.1	10
9	14	73	42.8	"drizzle"	"drizzle"	"drizzle"	"drizzle"	"drizzle"		"drizzle"	86.8	4.2	11
9	19	73	36.1			Yes	Yes				83.5	4.4	19
11	8	73	39.0		Yes			Yes	Yes	Yes 2	64.5	2.3	8
5	7	74	33.8			Yes	Yes				84.3	5.3	11
6	6	74	42.3		Yes	Yes	Yes	Yes	T. Precip		78.1	3.9	12
6	11	74	44.5			Yes	Yes	Yes			78.9	4.8	11
9	10	74	32.4		Yes	Yes	Yes	Yes	Yes	Yes	76.9	6.7	24
9	19	74	38.9	Yes	Yes	Yes	Yes	Yes	Yes		78.8	4.8	21
10	14	74	38.4	Yes	Yes	Yes	Yes	Yes	Yes 2	Yes 2	75.1	4.9	18

Notes:

a Fog forecast for early part of second day on 8:00 am to 8:00 am sampling schedule
b Data not immediately available
c Observed during early part of second day on 8:00 am to 8:00 am sampling schedule
d Fog observed during second day segment of sample - no time of observation given
e Observed in hours prior to beginning of sample
f No time indicated for observation (possible internal inconsistency in records)
g Fog prior to sample, trace precipitation or "drizzle" during sample
2 Heavy Fog

Relative humidity and ozone averages are taken for the 24 hour period corresponding to sulfate samples. Missing hourly data were replaced by linear interpolation between adjacent data points prior to averaging. 24 hour average relative humidity values are approximate since observations are taken for 14 hours daily, thus necessitating extensive interpolation.

T. Precip. - Trace of precipitation

Review of Table V shows that fog was forecast at some point in the Basin on all but 10 days of the 62 days of high sulfate values. Four of these remaining days contained forecasts for "drizzles" or "sprinkles", leaving only 6 days of high sulfate without a prior indication of high moisture concentrations. Of those 6 days, fog was observed on 3 days, even though not forecast; drizzle occurred on a fourth day, and a fifth day showed the highest average relative humidity of the entire 62-day sample population. On 29 days, fog was forecast for the immediate vicinity of the air monitoring station at downtown Los Angeles. Fog was observed at coastal airports near major SO_2 sources on 31 of the days in question, and other indicators of condensation such as trace precipitation or drizzles were observed on 10 additional days. In most cases the weather forecasts were for "late night and early morning low clouds and fog". While this is not a particularly uncommon forecast, high sulfate values are likewise common in the Los Angeles area. Oxidant levels on these days are quite variable: 9 days with instantaneous maximum over 0.20 ppm; 28 days between 0.20 and 0.10 ppm instantaneous maximum; 22 days when ozone levels never exceeded 0.10 ppm at any time at downtown Los Angeles.

The picture emerging from this analysis can be summarized as follows. Twenty-four hour average sulfate levels on the same day are nearly the same at coastal (Lennox), central city (Los Angeles), and suburban (Pasadena) locations along the direction of resultant pollutant transport, as would be predicted by the "dispersion cancels chemical reaction" approximation or by the passage over the Basin of a well-aged air mass containing sulfates. The most important phenomena explaining the large fluctuations in sulfate level from day to day are meteorological in nature. Low afternoon inversions concentrate sulfate pollutants near ground level. High relative humidity or fog seems to accelerate the conversion of SO_2 to form sulfate or to otherwise increase the total quantity of sulfate formed. In addition to this relative humidity effect, dependence of sulfate values on both photochemical indicators (ozone) and ambient particulate concentrations indicate that a variety of sulfate formation mechanisms, both homogeneous

gas-phase and heterophase particulate, are probably important in the Los Angeles atmosphere.

In Conclusion

Sulfur dioxide emission trends have been reviewed in relation to sulfur dioxide air quality in the Los Angeles area. Simple statistical tests indicate that measured SO_2 air quality levels at Long Beach and downtown Los Angeles track changes in emission strength at nearby sources and from sources with low effective stack height. These findings are consistent with the assumptions of conventional diffusion models. It thus seems likely that strategies aimed solely at control of ambient sulfur dioxide concentrations in Los Angeles may be analyzed successfully using commonly accepted engineering practices.

Fluctuations in measured sulfate values from day to day have been shown to track changes in inversion height, relative humidity, total suspended particulate levels and ozone concentrations. From these relationships, it is suggested that day-to-day fluctuations in sulfate concentration are driven mainly by changes in factors affecting SO_2 to sulfate reaction rate and by changes in the effective volume of the reactor. A variety of homogeneous gas-phase and heterogeneous particulate-phase reaction mechanisms are indicated, with possible additional complication by the intrusion of fog on days of high sulfate concentration. The effect of SO_2 source emission changes appears heavily masked by meteorological and co-pollutant variations from day to day as indicated in Table III by the ability to explain much of the behavior of four years of recent sulfate data, without consideration of sizable summer/winter changes in SO_2 emission strength. The relationship between SO_2 emission changes and spatially resolved sulfate air quality requires much further work.

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APPENDIX I

SULFUR DIOXIDE EMISSIONS IN LOS ANGELES COUNTY
(tons per day)

YEAR	STEAM POWER PLANTS	PETROLEUM REFINING (a)	CHEMICAL PLANTS (b)	MOTOR VEHICLES (c)	OTHER SOURCES (d)	TOTAL	REMARKS
1956	187 (47)(e)	179	45	36	289	736	
1957	240 (57)	50	46	35	174	545	
1958	122 (66)	50	47	35	199	453	
1959	150 (64)			30			
1960	153 (65)	40	51	25	49	318	
1961	132 (71)	36	52	27	46	293	
1962	120 (75)			26			
1963	108 (78)			25			
1964	116 (77)	45	65	24	33	283	
1965	136 (76)			23			
1966	192 (76)	35	65	25	35	352	
1967	145 (76)			26			Low sulfur oil became available.
1968	82 (84)	55	90	26	39	292	
1969	57 (79)			27			
1970	42 (77)	50	115	27	16	250	
1971	76 (77)			28			
1972	83 (58)			29			
1973	161 (30)	55	60	30	59	365	
1974	115 (31)	58	20	30	33	256	Appreciable supplies of hydroelectric power was imported in 1974. Not expected in the future.
1975	190 (7)			31			
1976	210 (.3)		11	31			
1977	220 (.3)			32			
1978	240 (0)			32			
1979	250 (0)	60	11	33	95(f)	~450	1979 & 1980 should have highest emissions of SO_2.
1980	250 (0)			33			
1981	245 (0)			33			Additional supplies of imported electricity will result in reduction of emissions, even though demand continues to grow.
1982	230 (0)			34			
1983	210 (0)	60	11	34	95(f)	410	

(a) Includes only those emissions from the refining operations. Does not include emissions from the combustion of fuels at the refinery location, i.e., from fired heaters, boilers, etc.

(b) Includes emissions from sulfur recovery plants and sulfuric acid plants.

(c) Includes only those emissions from gasoline-powered motor vehicles. Does not include emissions from aircraft and diesel-powered motor vehicles.

(d) Includes SO_2 emissions from combustion of fuels in all sources other than steam electric power plants and gasoline-powered motor vehicles. Also includes SO_2 emissions from metallurgical processes, incineration of refuse and other minor sources.

(e) Parentheses indicates percent level of service of natural gas.

(f) The forecasted increase is based upon substitution of low sulfur oil for all natural gas burned in refineries and substitution of low sulfur oil for ½ of the natural gas burned in industry. Fuel usage figures for 1974 were used as a basis for fuel consumption from refineries and industry between 1980 and 1983. No growth in fuel use for these industries could be predicted because an actual fuel reduction of about 15 percent occurred between 1970 and 1974.

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APPENDIX II

Nomenclature for Appendix II

Symbol	Description	Units in Which Value is Stated	Averaging Time
SO_4	Water soluble sulfate ion concentration extracted from hi vol filter	$\mu gm/m^3$	24 hr
Inv. Max.	Height of afternoon inversion base over downtown LA (estimated from morning sounding)[b]	100's ft above msℓ	
Inv. Base	Height of early morning inversion base at LA Int'l Airport[b]	100's ft above msℓ	
Wind Sp	Scalar average wind speed at downtown LA	mph	24 hr
Sol Rad	Solar radiation intensity at downtown LA	$\frac{gm\ cal}{cm^2\ hr}$	24 hr
Max Temp	Maximum temperature reached at downtown LA	^oF	
O3 Max	Instantaneous maxima of daily oxidant observations at downtown LA	pphm	
Avg O3	Average of daily oxidant observations at downtown LA	ppm	24 hr
NO_2	Average of daily NO_2 observations at downtown LA	ppm	24 hr
Total HC	Average of daily total hydrocarbon observations at downtown LA	ppm	24 hr
SO_2	Average of daily SO_2 observations at downtown LA	ppm	24 hr
TSP	Total suspended particulate concentration at downtown LA	$\mu gm/m^3$	24 hr
(1-RH)	One minus the average of relative humidity observations at downtown LA. Relative humidity expressed in percent/100		24 hr

Notes: (a) Averages are taken for the 24 hour period corresponding to the sulfate sample schedule. Missing hourly data were replaced by linear interpolation between adjacent data points prior to averaging. 24 hour average relative humidity values are approximate since observations are taken for 14 hours daily, thus necessitating extensive interpolation.
(b) Detailed estimates of mixing depth for observations with inversion height above 5000 ft are not available. Mixing depth on those occasions will be estimated as 6667 ft.

Statistical Description of Data Base
Used in Study of Sulfate Correlation with Meteorological and Pollutant Variables

A. Data Base Incorporating all Complete Sets of Observations

Sampling Station is Downtown Los Angeles

Number of Complete Sets of Observations = 342

Time Period Spanned is August 1965 through December 1974

	Variable												
	$SO_4^=$	Inv Max	Inv Base	Wind Speed	Solar Rad	Max Temp	Ozone Max	Avg Ozone	NO_2	Total Hydrocarbons	SO_2	TSP	(1-RH)
Average	13.97	40.57	18.51	5.36	18.48	75.72	11.77	0.032	0.083	3.32	0.019	157.26	0.36
Standard Deviation	11.60	17.09	19.55	1.19	6.80	10.08	7.67	0.017	0.039	1.11	0.007	59.20	0.17

Linear Correlation Between Variables

$SO_4^=$	1.00	-0.55	-0.04	-0.04	-0.04	-0.07	0.09	0.18	0.11	-0.06	0.25	0.31	-0.49
Inv Max	-0.55	1.00	0.30	0.11	-0.16	-0.15	-0.24	-0.29	-0.12	-0.08	-0.27	-0.32	0.46
Inv Base	-0.04	0.30	1.00	0.45	-0.08	-0.39	-0.36	-0.24	-0.46	-0.47	-0.39	-0.37	-0.26
Wind Sp	-0.04	0.11	0.45	1.00	0.31	-0.10	-0.17	-0.03	-0.51	-0.58	-0.42	-0.39	-0.06
Sol Rad	-0.04	-0.16	-0.08	0.31	1.00	0.42	0.45	0.51	-0.15	-0.13	-0.10	-0.10	0.02
Max Temp	-0.07	-0.15	-0.39	-0.10	0.42	1.00	0.59	0.52	0.24	0.25	0.19	0.16	0.33
O3 Max	0.09	-0.24	-0.36	-0.17	0.45	0.59	1.00	0.92	0.34	0.33	0.22	0.32	0.11
Avg O3	0.18	-0.29	-0.24	-0.03	0.51	0.52	0.92	1.00	0.17	0.17	0.10	0.22	-0.02
NO_2	0.11	-0.12	-0.46	-0.51	-0.15	0.24	0.34	0.17	1.00	0.73	0.49	0.64	0.27
Total HC	-0.06	-0.08	-0.47	-0.58	-0.13	0.25	0.33	0.17	0.73	1.00	0.42	0.61	0.31
SO_2	0.25	-0.27	-0.39	-0.42	-0.10	0.19	0.22	0.10	0.49	0.42	1.00	0.47	0.04
TSP	0.31	-0.32	-0.37	-0.39	-0.10	0.16	0.32	0.22	0.64	0.61	0.47	1.00	0.09
(1-RH)	-0.49	0.46	-0.26	-0.06	0.02	0.33	0.11	-0.02	0.27	0.31	0.04	0.09	1.00

Correlation Between Natural Log of Variables

$SO_4^=$	1.00	-0.60	0.26	-0.03	-0.03	0.009	0.22	0.31	0.14	-0.01	0.22	0.38	-0.50
Inv Max	-0.60	1.00	-0.02	0.09	-0.12	-0.12	-0.32	-0.33	-0.16	-0.10	-0.29	-0.35	0.44
Inv Base	0.26	-0.02	1.00	0.48	0.02	-0.24	-0.21	-0.02	-0.50	-0.55	-0.35	-0.33	-0.48
Wind Sp	-0.03	0.09	0.48	1.00	0.36	-0.05	-0.12	0.04	-0.56	-0.63	-0.45	-0.44	-0.09
Sol Rad	-0.03	-0.12	0.02	0.36	1.00	0.37	0.57	0.57	-0.09	-0.08	-0.06	-0.03	0.16
Max Temp	0.009	-0.12	-0.24	-0.05	0.37	1.00	0.49	0.45	0.20	0.21	0.16	0.15	0.27
O3 Max	0.22	-0.32	-0.21	-0.12	0.57	0.49	1.00	0.91	0.30	0.27	0.24	0.35	0.04
Avg O3	0.31	-0.33	-0.02	0.04	0.57	0.45	0.91	1.00	0.15	0.10	0.13	0.24	-0.06
NO_2	0.14	-0.16	-0.50	-0.56	-0.09	0.20	0.30	0.15	1.00	0.70	0.47	0.66	0.25
Total HC	-0.01	-0.10	-0.55	-0.63	-0.08	0.21	0.27	0.10	0.70	1.00	0.43	0.62	0.27
SO_2	0.22	-0.29	-0.35	-0.45	-0.06	0.16	0.24	0.13	0.47	0.43	1.00	0.48	0.04
TSP	0.38	-0.35	-0.33	-0.44	-0.03	0.15	0.35	0.24	0.66	0.62	0.48	1.00	0.10
(1-RH)	-0.50	0.44	-0.48	-0.09	0.16	0.27	0.04	-0.06	0.25	0.27	0.04	0.10	1.00

Statistical Description of Data Base
Used in Study of Sulfate Correlation with Meteorological and Pollutant Variables

B. Data Base Incorporating Observations Since Change in Sampling Schedule of September, 1970

Sampling Station is Downtown Los Angeles

Number of Complete Sets of Observations = 186

Time Period is September 1970 through December 1974

	Variable												
	$SO_4^=$	Inv Max	Inv Base	Wind Speed	Solar Rad	Max Temp	Ozone Max	Avg Ozone	NO_2	Total Hydrocarbons	SO_2	TSP	(1-RH)
Average	16.15	40.84	20.15	5.56	17.49	75.46	9.67	0.028	0.081	3.15	0.019	151.19	0.36
Standard Deviation	13.11	16.67	20.19	1.31	6.68	11.12	6.52	0.015	0.039	1.04	0.008	61.26	0.16

Linear Correlation Between Variables

$SO_4^=$	1.00	-0.54	-0.05	-0.13	-0.04	-0.13	-0.13	-0.19	-0.12	-0.007	0.34	0.33	-0.55
Inv Max	-0.54	1.00	0.35	0.20	-0.09	-0.14	-0.23	-0.22	-0.19	-0.16	-0.39	-0.35	0.40
Inv Base	-0.05	0.35	1.00	0.44	-0.20	-0.38	-0.41	-0.25	-0.45	-0.45	-0.38	-0.37	-0.26
Wind Sp	-0.13	0.20	0.44	1.00	0.27	-0.05	-0.14	0.02	-0.47	-0.56	-0.39	-0.35	0.06
Sol Rad	-0.04	-0.09	-0.20	0.27	1.00	0.50	0.51	0.55	-0.12	-0.11	-0.06	-0.09	0.11
Max Temp	-0.13	-0.14	-0.38	-0.05	0.50	1.00	0.59	0.50	0.18	0.14	0.17	0.06	0.35
O3 Max	0.13	-0.23	-0.41	-0.14	0.51	0.59	1.00	0.91	0.24	0.20	0.26	0.18	0.15
Avg O3	0.19	-0.22	-0.24	0.02	0.55	0.50	0.91	1.00	0.02	-0.03	0.12	0.02	0.01
NO_2	0.12	-0.19	-0.45	-0.47	-0.12	0.18	0.24	0.02	1.00	0.77	0.51	0.68	0.25
Total HC	-0.007	-0.16	-0.45	-0.56	-0.11	0.14	0.20	-0.03	0.77	1.00	0.42	0.67	0.27
SO_2	0.34	-0.39	-0.38	-0.39	-0.06	0.17	0.26	0.12	0.51	0.42	1.00	0.50	-0.06
TSP	0.33	-0.35	-0.37	-0.35	-0.09	0.06	0.18	0.02	0.68	0.67	0.50	1.00	0.08
(1-RH)	-0.55	0.40	-0.26	0.06	0.11	0.35	0.15	0.01	0.25	0.27	-0.06	0.08	1.00

Correlation Between Natural Log of Variables

$SO_4^=$	1.00	-0.62	0.27	-0.09	-0.007	-0.10	0.26	0.32	0.08	0.004	0.37	0.35	-0.66
Inv Max	-0.62	1.00	0.07	0.19	-0.07	-0.08	-0.33	-0.26	-0.21	-0.14	-0.42	-0.39	0.40
Inv Base	0.27	0.07	1.00	0.43	-0.13	-0.25	-0.34	-0.09	-0.50	-0.51	-0.31	-0.37	-0.51
Wind Sp	-0.09	0.19	0.43	1.00	0.31	0.01	-0.10	0.12	-0.52	-0.61	-0.42	-0.41	0.01
Sol Rad	-0.007	-0.07	-0.13	0.31	1.00	0.38	0.59	0.58	-0.05	-0.05	-0.03	-0.01	0.22
Max Temp	0.10	-0.08	-0.25	0.01	0.38	1.00	0.43	0.37	0.13	0.12	0.13	0.04	0.28
O3 Max	0.26	-0.33	-0.37	-0.10	0.59	0.43	1.00	0.89	0.24	0.20	0.32	0.26	0.07
Avg O3	0.32	-0.26	-0.09	0.12	0.58	0.37	0.89	1.00	0.00	-0.05	0.15	0.06	-0.06
NO_2	0.08	-0.21	-0.50	-0.52	-0.05	0.13	0.24	0.00	1.00	0.71	0.51	0.69	0.27
Total HC	0.004	-0.14	-0.51	-0.61	-0.05	0.12	0.20	-0.05	0.71	1.00	0.42	0.67	0.28
SO_2	0.37	-0.42	-0.31	-0.42	-0.03	0.13	0.32	0.15	0.51	0.42	1.00	0.54	-0.08
TSP	0.35	-0.39	-0.37	-0.41	-0.01	0.04	0.26	0.06	0.69	0.67	0.54	1.00	0.09
(1-RH)	-0.66	0.40	-0.51	0.01	0.23	0.28	0.07	-0.06	0.27	0.28	-0.08	0.09	1.00